

Ferroelectric thin films properties: depolarization field and Landau free-energy coefficients renormalization

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Abstract

The calculation of the polarization in ferroelectric thin films is performed using an analytical solution of the Euler-Lagrange differential equation with boundary conditions with different extrapolation lengths of positive sign on the surfaces. The depolarization field effect is taken into account in the model for a short-circuited single domain film, that is a perfect insulator. It is shown that the calculation of the polarization and other properties profiles and average values can be reduced to the minimization of the free energy expressed as a power series of the average polarization with a renormalized coefficient which depends on temperature, film thickness, extrapolation lengths, and a coefficient for the polarization gradient term in the free energy functional, the depolarization field being also included into the renormalized coefficient. The function defining the space distribution properties is calculated as well and its amplitude is shown to coincide with the average polarization. The detailed calculations of the spontaneous polarization, dielectric susceptibility and pyrocoefficient is performed. The divergence of the dielectric susceptibility and pyrocoefficient for critical parameters of the thickness induced ferroelectric

phase transition, namely at temperature T_{cl} and critical length l_c , is shown to exist with and without the depolarization field contribution, although the values of T_{cl} and l_c are different in both cases. The detailed analysis of the depolarization field space distribution and of this field dependence on temperature and film thickness is performed.

I. INTRODUCTION

The non homogeneity of the polarization and other properties is known to be a characteristic feature of ferroelectric thin films. The physical reason of this phenomenon is related to the influence of the films surface, where, e.g., the polarization differs essentially from that in the bulk. Because of this polarization heterogeneity, the phenomenological approach to its calculation was based on the solution of Euler-Lagrange and Lamé type differential equations respectively for polarization and dielectric susceptibility with specific boundary conditions [1,2]. Because the analytical solution of these equations appeared to be cumbersome, their solution was performed numerically in most of the papers, mainly for BaTiO_3 and PbTiO_3 (see e.g. [3,4,5]). Therefore the analytical calculations of the film properties appeared to be more complex than in bulk materials, where the minimization of the free energy as a power series of homogeneous polarization makes it possible to calculate the properties analytically by a simple way. The real situation in films is even more complex because of the depolarization field contribution, which, contrary to the bulk, is non zero even in short circuited films because of the polarization non homogeneity. Although the depolarization field is able to completely destroy ferroelectric polarization [6] there are only a few works devoted to calculations of its contribution to the film properties [7]. The majority of the authors performed the calculations without taking into account the depolarization field effect [3,4,5]. It might be supposed that the flattening of the polarization via the depolarization field contribution, as shown in [7], could create conditions for a simplification of the thin film properties description, particularly on the basis of a free energy expansion similar to that in

bulk materials, but with renormalized coefficients. Such approach was successfully applied recently to the description of thin films [8] and nanomaterials [9]. However, up to now, there was no fundamental background for such a simplified approach. In addition, nothing was discussed about the properties profiles, which cannot be obtained from conventional expansion of the free energy as a power series of the polarization.

In the present work we show for the first time that polarization and other properties averaged over the film thickness can be found by the minimization of the free energy with the same form as known for the bulk materials, but with the coefficient before square polarization depending upon temperature and film thickness, and featuring the extrapolation length and coefficient before polarization gradient. The space distribution of the polarization is calculated using the analytical solution of the Euler-Lagrange equation. The amplitude of this distribution is shown to be equal to the average polarization with a good accuracy and can thus be obtained from the aforementioned free energy. The depolarization field contribution is taken into account in the model which was proposed in [7] for single domain ferroelectric films under short circuit conditions, ferroelectric treated as a perfect insulator. This model seems to be reasonable because the thinner the film the better the conditions for single domain state appearance (see e.g. [2], [10]). In addition, for many perovskite ferroelectrics, the conductivity can be small enough [11]. To analyze the depolarization field effect we perform a detailed comparison of the properties calculated with and without taking into account the depolarization field.

II. BASIC EQUATIONS

Let us consider a thin ferroelectric film polarized along the z -axis (i.e. $P_z \neq 0$, $P_x = P_y = 0$), which is perpendicular to the surface of the film. This type of polarization can appear as a result of self-polarization of a film grown under special technological condition without application of any external electric field [12,13]. Since the type of substrate and electrode was shown to be important, the mechanical strain related to the mismatch of the substrate

and the film lattice constants and the thermal expansion coefficients can contribute to a self-polarization phenomenon.

The polarization equilibrium value can be obtained in the framework of the phenomenological thermodynamic theory from the minimum of the functional of the free energy [14]. In the considered case of polarization perpendicular to the surface of the film, it is necessary to take into account the depolarization field, which is proportional to the value of polarization and has the opposite direction, in such a way that it lowers or even cancels P_s . In accepted models, the ferroelectric is regarded as a perfect insulator under short-circuit conditions. Taking into account the symmetry of the considered structure (i.e. the film polarization depends on the coordinate z only) one can write the free energy density functional for phase transitions of the 1st and 2nd order ($\gamma \neq 0$ and $\gamma = 0$ respectively) as follows:

$$F = \frac{1}{l} \int_0^l \left[\frac{\alpha}{2} P_z^2(z) + \frac{\beta}{4} P_z^4(z) + \frac{\gamma}{6} P_z^6(z) + \frac{\delta}{2} \left(\frac{dP_z(z)}{dz} \right)^2 - E_z P_z(z) \right] dz + \quad (1)$$

$$+ \frac{\delta}{2l} \left(\frac{P_z^2(0)}{\lambda_1} + \frac{P_z^2(l)}{\lambda_2} \right) + 2\pi \left[\frac{1}{l} \int_0^l P_z^2(z) dz - \left(\frac{1}{l} \int_0^l P_z^2(z) dz \right)^2 \right].$$

Here l is the thickness of the film, the coefficient α depends on temperature T as $\alpha = \alpha_0(T - T_c)$, T_c is the temperature of the transition from paraelectric to ferroelectric phase in the bulk ferroelectric, E_z is the external electric field, $\lambda_{1,2}$ are extrapolation lengths. The last two and the previous two terms represent the depolarization field energy and surface energy respectively. In what follows we will consider the case of positive extrapolation lengths, i.e., when polarization on the surface is smaller then in the center of the film. Only in this case surface effects can lead to a size-driven phase transition [1].

The minimization of the functional (1) leads to the following equation determining the space distribution of polarization over the thickness of the film:

$$\alpha P_z + \beta P_z^3 + \gamma P_z^5 - \delta \frac{d^2 P_z}{dz^2} = E_z - 4\pi P_z + 4\pi \frac{1}{l} \int_0^l P_z dz \quad (2a)$$

with boundary conditions on the surfaces of the film:

$$\left(\lambda_1 \frac{dP_z}{dz} - P_z \right) \Big|_{z=0} = 0, \quad \left(\lambda_2 \frac{dP_z}{dz} + P_z \right) \Big|_{z=l} = 0. \quad (2b)$$

The last two terms in Eq. (2a) represent the depolarization field:

$$E_z^d = -4\pi \left(P_z - \frac{1}{l} \int_0^l P_z dz \right). \quad (3)$$

Here the first term is the depolarization field for the free standing film, and the second one is the compensating field of free charges on the short-circuiting electrodes. The depolarization field (3) is of course zero when the polarization space distribution is homogeneous.

III. CRITICAL TEMPERATURE AND THICKNESS OF THE SIZE-DRIVEN PHASE TRANSITION

Equation (2a) for the polarization space distribution is a non-linear inhomogeneous integral differential equation and is cumbersome to solve analytically. But in the paraelectric phase, where the spontaneous polarization P_s equals zero and the polarization is only proportional to the external field, the non-linear terms in Eq. (2a) can be negligibly small.

Therefore the solution of this linear equation can be expressed in terms of elementary functions. With boundary conditions (2b), the space distribution of the polarization in this case has the following form:

$$\begin{aligned} P^{PE}(\xi) &= \frac{1 - \varphi(\xi)}{4\pi(\Phi - f)} E; \\ \varphi(\xi) &= \frac{(1 + d_2 - (1 - d_1) \exp(-h)) \exp(-\xi) + (1 + d_1 - (1 - d_2) \exp(-h)) \exp(\xi - h)}{(1 + d_1)(1 + d_2) - (1 - d_1)(1 - d_2) \exp(-2h)}; \quad (4) \\ \Phi = \langle \varphi \rangle &= \frac{1 - \exp(-h)}{h} \frac{2 + d_1 + d_2 - (2 - d_1 - d_2) \exp(-h)}{(1 + d_1)(1 + d_2) - (1 - d_1)(1 - d_2) \exp(-2h)}. \end{aligned}$$

Here all 'z' indexes are omitted, angle bracket means z coordinate averaging and the following definitions are introduced:

$$\xi = \sqrt{1 - f} \frac{z}{l_0}; \quad f = \frac{-\alpha}{4\pi}; \quad l_d^2 = \frac{\delta}{4\pi}; \quad d_i = \sqrt{1 - f} \frac{\lambda_i}{l_d}; \quad h = \sqrt{1 - f} \frac{l}{l_d}. \quad (5)$$

The average polarization of the film can be easily derived from (4):

$$\langle P^{PE} \rangle = \frac{1 - \Phi}{4\pi(-f + \Phi)} E. \quad (6)$$

Note that in the case $d_1 = d_2$ the space distribution of the polarization in the paraelectric phase (4) and its average value (6) coincides with those obtained earlier [7].

The derivative $\chi = (dP/dE)|_{E=0}$ represents the linear dielectric susceptibility of the film. The analysis of expression (6) has shown that the value of χ is positive when either $f < 0$ (i.e. $\alpha > 0$, $T > T_c$ - paraelectric phase of bulk ferroelectrics) or $f > 0$ and $\Phi > f$ ($T < T_c$ - ferroelectric phase of bulk ferroelectrics). The dielectric susceptibility diverges for $\Phi = f$, and the considered system undergoes a phase transition.

Because of the f and Φ dependences on thickness and temperature, equation $\Phi = f$ determines accordingly the critical temperature T_{cl} at fixed thickness or critical thickness l_c at fixed temperature.

Note that these critical parameters correspond to the points where the ferroelectric phase loses its stability (1st order phase transition) or to the critical temperature and thickness for a 2nd order ferroelectric phase transition. The parameters f and l_d can be estimated respectively as $1/\varepsilon$ and $r_c/\sqrt{\varepsilon}$ where ε and r_c are the dielectric permittivity and correlation radius of the bulk ferroelectric in the paraelectric phase respectively. Therefore for conventional values of these quantities $f \ll 1$ and $l/l_d \approx h \gg 1$. These inequalities essentially simplify the form of $\varphi(\xi)$ and Φ so the equation determining the phase transition point can be rewritten as follows:

$$h = \frac{U_1 + U_2}{f}, \quad U_i = \frac{1}{1 + d_i}. \quad (7)$$

The critical thickness is readily obtained from this expression:

$$l_c = \frac{U_1 + U_2}{f} l_d = \frac{4\pi}{-\alpha} \sqrt{\frac{\delta}{4\pi}} \left[\left(\lambda_1 \sqrt{\frac{4\pi}{\delta}} + 1 \right)^{-1} + \left(\lambda_2 \sqrt{\frac{4\pi}{\delta}} + 1 \right)^{-1} \right], \quad (8)$$

and the critical temperature

$$T_{cl} = T_c \left[1 - \frac{l_0^2(0)}{l} \left(\frac{1}{\lambda_1 + l_d} + \frac{1}{\lambda_2 + l_d} \right) \right], \quad l_0(0) = \sqrt{\frac{\delta}{\alpha_0 T_c}}. \quad (9)$$

Here $l_0(0)$ is the correlation length at zero temperature. As it follows from Eq. (9), if the thickness value is less than $l_c(0) = l_0^2(0)/((\lambda_1 + l_d)^{-1} + (\lambda_2 + l_d)^{-1})$, then the critical temperature becomes negative, i.e. phase transition vanishes.

Therefore the ferroelectric phase transition in a film can be achieved by changing the film thickness at some fixed temperature or by varying the temperature of the film with given thickness. As a matter of fact the curve described by equation (9) determines the phase boundaries between the paraelectric and ferroelectric phases, i.e. the phase diagram of the film in temperature - thickness coordinates, which is depicted in Fig.1 by solid curves for different values of the extrapolation lengths. The critical thickness values $l_c(0)$ are the intersections of the curves with the abscissa axis. Namely, at $l < l_c(0)$, the paraelectric phase (polarization $P_s = 0$) exists in the whole temperature region, while at $l > l_c(0)$ both ferroelectric phase ($P_s \neq 0$) at $T < T_{cl}$ and paraelectric phase at $T > T_{cl}$ are present. It should be noticed that paraelectric and ferroelectric phases should coexist in the FE region of Fig. 1 for first order phase transitions. To clear up the effect of the depolarization field we also conducted calculations without any depolarization field contribution. The results of the calculations of T_{cl} and l_c for 2nd order phase transitions are given in the Appendix (Eqs. (A5), (A6)) and in Fig. 1 (dashed curves).

It is seen from Fig. 1 that the depolarization field decreases the critical temperature and increases the critical thickness. These effects are stronger when decreasing the extrapolation lengths values (compare solid and dashed curves in Fig.1). It is clearly seen, from the inset of Fig. 1, that $(T_c - T_{cl}) \sim 1/l$ (solid curves), while without the depolarization field contribution $(T_c - T_{cl}) \sim 1/l^2$ (dashed curves). A more detailed critical thickness dependence on the extrapolation lengths is represented in Fig. 2. One can see that the greater the d_1 and d_2 values, the smaller the l_c value. The latter can be related to the flattening of the polarization space distribution on increasing the values of the extrapolation lengths, that results into a critical thickness decrease and in a critical temperature increase (compare curves 1, 2 and 3 in Fig.1).

When inequalities $\Phi < f$ and $f > 0$ are valid, the polarization derived by equation (4) becomes negative, and the non-linearity in equation (2a) cannot be neglected.

IV. THE FREE ENERGY

In the ferroelectric phase (the region $l > l_c(0)$ and $T < T_d$) the non-linearity should be taken into consideration. The simplest way to take it into account is the direct variational method. We choose solution (4) as a trial function and an amplitude factor will be treated as a variational parameter. The condition of FE existence $h \geq (U_1 + U_2)/f$ can be fulfilled because of small f and l_d values. Allowing for $h \gg 1$ we will look for a polarization space distribution in the ferroelectric phase with the following form:

$$P^{FE}(\xi) = P(1 - \varphi(\xi)), \quad \varphi(\xi) = \begin{cases} U_1 \exp(-\xi), & 0 \leq \xi \ll h/2; \\ 0, & \xi \sim h/2; \\ U_2 \exp(\xi - h), & 0 \leq h - \xi \ll h/2. \end{cases} \quad (10)$$

Here P is the variational parameter that represents the amplitude of the polarization space distribution.

After calculation of integral (1) with the trial function (10), one can easily obtain the free energy density as follows:

$$F = \alpha \left(1 - \frac{A_1}{f}\right) (1 - A_1) \frac{P^2}{2} + \beta(1 - B) \frac{P^4}{4} + \gamma(1 - C) \frac{P^6}{6} - EP(1 - A_1) \quad (11a)$$

Keeping in mind that the polarization average value is $\langle P \rangle = P(1 - A_1)$ one can rewrite Eq.(11a) as:

$$F = \alpha \frac{(1 - A_1/f) \langle P \rangle^2}{1 - A_1} + \beta \frac{(1 - B) \langle P \rangle^4}{(1 - A_1)^4} + \gamma \frac{1 - C}{(1 - A_1)^6} \frac{\langle P \rangle^6}{6} - E \langle P \rangle. \quad (11b)$$

where the following definitions have been used

$$A_1 = \frac{U_1 + U_2}{h}, \quad B = \frac{G(U_1) + G(U_2)}{12h}, \quad C = \frac{Q(U_1) + Q(U_2)}{60h}, \quad (12)$$

$$G(U_i) = 48U_i - 36U_i^2 + 16U_i^3 - 3U_i^4,$$

$$Q(U_i) = 360U_i - 450U_i^2 + 400U_i^3 - 225U_i^4 + 72U_i^5 - 10U_i^6$$

It is worth to underline that the terms in Eq. (1) which correspond to surface energy, depolarizing field and polarization gradient contribute to the first term in Eqs. (11). Therefore the main peculiarities of thin film properties have to be related to the coefficient of the second power of the polarization.

It can be seen that Eqs. (11a) and (11b) have the form of power series of the amplitude of the polarization space distribution and average polarization respectively. These equations can be easily rewritten in the conventional for bulk ferroelectric form

$$F = a \frac{P^2}{2} + b \frac{P^4}{4} + c \frac{P^6}{6} - E' P \quad (13a)$$

and

$$F = a_1 \frac{\langle P \rangle^2}{2} + b_1 \frac{\langle P \rangle^4}{4} + c_1 \frac{\langle P \rangle^6}{6} - E \langle P \rangle, \quad (13b)$$

where the coefficients a , b , c and a_1 , b_1 , c_1 can be obtained from the comparison of Eqs. (11a,b) and (13a,b), namely

$$a = \alpha \left(1 - \frac{A_1}{f} \right) (1 - A_1), \quad b = \beta(1 - B), \quad c = \gamma(1 - C), \quad E' = E(1 - A_1) \quad (14a)$$

and

$$a_1 = \frac{\alpha(1 - A_1/f)}{1 - A_1}, \quad b_1 = \frac{\beta(1 - B)}{(1 - A_1)^4}, \quad c_1 = \frac{\gamma(1 - C)}{(1 - A_1)^6}. \quad (14b)$$

In the general case, the coefficients (14a,b) depend on the temperature, the film thickness, the extrapolation lengths and the coefficient before polarization gradient, as it follows from Eqs. (12), (7) and (5). At first glance these dependencies seem to be rather complex, although they have been already simplified due to inequalities $f = 1/\varepsilon \ll 1$, $h = l/l_d \gg 1$. A further simplification of the coefficients (14) was made by rewriting them via the critical temperature $T_{cl} = T_c - (U_1 + U_2)/\alpha_0 \cdot 4\pi l_d/l$ or via the critical thickness $l_c/l_d = (U_1 + U_2)4\pi/(\alpha_0(T_c - T))$ (see the left hand side part of Eq. (8)). The first or the second type of the coefficients representation can be useful when studying respectively the temperature (at given thickness) or thickness (at fixed temperature) dependencies of the film properties. In the first case the coefficients a in (14a) and a_1 in (14b) can be rewritten as:

$$a = \alpha_0(T - T_{cl}) \left[1 - \frac{\alpha_0}{4\pi}(T_c - T_{cl}) \right] \quad (15a)$$

and

$$a_1 = \alpha_0(T - T_{cl}) \frac{1}{1 - \frac{\alpha_0}{4\pi}(T_c - T_{cl})}. \quad (15b)$$

An estimation of the second multipliers in Eqs. (15a) and (15b) has shown that they are very close to unity (for ferroelectric phase transition of displacement type $\alpha_0/(4\pi) \leq 10^{-5}$ with $T_c - T_{cl} \leq 10^2$ and for order-disorder type $\alpha_0/(4\pi) \approx 10^{-3}$ with $T_c - T_{cl} < 10^2$) and so $1 - A_1 \approx 1$ everywhere in Eqs. (14a) and (14b). Similar estimations have shown that $B \ll 1$ and $C \ll 1$ so that with a good accuracy

$$a = a_1 = \alpha_0(T - T_{cl}), \quad b = b_1 = \beta, \quad c = c_1 = \gamma, \quad E' = E. \quad (16a)$$

When studying the thickness dependence of the film properties at fixed temperature, substitution of critical thickness $l_c(8)$ into Eq. (14) yields:

$$a = a_1 = K \frac{l_d}{l_c} \left(\frac{l_c}{l} - 1 \right), \quad K \equiv (U_1 + U_2)4\pi, \quad (16b)$$

the coefficients b , b_1 , c , c_1 and E' being the same as in (16a). We should underline once more that the critical temperature T_{cl} depends on l and the critical thickness l_c depends on T , and both of them are functions of the extrapolation lengths and parameter δ (see Figs. 1, 2 and Eqs. (8), (9)), the contribution of depolarizing field also being included. Because of that, all the physical properties (polarization, dielectric susceptibility, pyrocoefficient, entropy, thermal capacity etc.), which can be obtained from conventional minimization of Eqs. (13a), (13b), have to be dependent on the aforementioned characteristics.

It should be also underlined, that Eqs. (13a), (13b) and (16a), (16b) are valid both in paraelectric ($T > T_{cl}$, $l < l_c$) and ferroelectric ($T < T_{cl}$, $l > l_c$) phases. This is because we chose the trial function for the description of the polarization profile in the form obtained for the paraelectric phase (see Eq. (4)) and used the inequality $h \gg 1$, $f \ll 1$, which are valid practically for any thin film, as discussed earlier.

Since the formulas which express the physical properties via the free energy coefficients for both first and second order phase transitions are of the common knowledge (see e.g. [15]), we shall consider only polarization, dielectric susceptibility and pyrocoefficients with special

attention to their thickness and temperature dependencies, which are the characteristic features of ferroelectric thin films. For sake of simplicity, we shall represent, in what follows, these dependencies for the second order phase transition. Special attention will be payed to depolarization field contribution to find out the cases and conditions at which these field effects are more or less important qualitatively or quantitatively.

V. THE SPECIFIC BEHAVIOR OF THE PHYSICAL PROPERTIES OF FERROELECTRIC THIN FILMS

A. The space distributions of the physical properties

The profiles of the physical properties are defined by the function $(1 - \varphi(\xi))$ in Eq. (10) and their amplitudes can be found by conventional minimization of free energy (13a) with the coefficients (16a), (16b). More particularly, for second order phase transitions at $E = 0$:

$$P = \sqrt{-\frac{\alpha_0(T - T_{cl})}{\beta}}, \quad \chi = \frac{1}{2\alpha_0(T_{cl} - T)}, \quad \Pi = \frac{\alpha_0}{\beta 2P} = \frac{\sqrt{\alpha_0}}{\sqrt{\beta 2\sqrt{T_{cl} - T}}}; \quad (17a)$$

$$P = \sqrt{\frac{K}{\beta} \frac{l_d}{ll_c} (l - l_c)}, \quad \chi = \frac{1}{2Kl_d/l_c(1 - l_c/l)}, \quad \Pi = \frac{\alpha_0}{2\sqrt{\beta} \sqrt{Kl_d/l_c(1 - l_c/l)}} \quad (17b)$$

for the ferroelectric phase ($T < T_{cl}$, $l > l_c$) and

$$P = 0, \quad \chi = \frac{1}{\alpha_0(T - T_{cl})}, \quad \Pi = 0; \quad (18a)$$

$$P = 0, \quad \chi = \frac{1}{Kl_d/l_c(l_c/l - 1)}, \quad \Pi = 0 \quad (18b)$$

for the paraelectric phase ($T > T_{cl}$, $l < l_c$).

Here P , χ and Π are the amplitudes of the polarization, dielectric susceptibility and pyrocoefficient which have to be multiplied by $(1 - \varphi(\xi))$ to obtain these properties profiles. The formulas (17a), (18a) and (17b), (18b) can be applied when studying respectively temperature (at fixed film thickness) and thickness (at fixed temperature) dependencies.

The space distributions of these quantities are depicted in Figs. 3, 4, 5 for several film thickness at fixed low temperature, P_{s0} , χ_0 , Π_0 being the quantities value at $l \rightarrow \infty$ (see Eq. (17b)). One can see that the amplitude of the susceptibility increases much faster than that of the pyrocoefficient at $l \rightarrow l_c$ while the amplitude of spontaneous polarization decreases with the decrease of the film thickness, the shape of all these quantities profiles being completely the same. It should be underlined that the profiles are asymmetrical for different extrapolation lengths on the two surfaces. It can be easily seen that the profiles remain smooth in the most part of the film even for thin films with thickness close to the critical value l_c (see solid curves 1 and 2). This phenomenon can be explained by the influence of the depolarization field that tends to flatten the polarization space distribution as it will be shown later.

B. The average values of the physical properties

The thickness and temperature dependencies of the properties can be obtained directly by minimization of the free energy (13b) with respect to Eqs. (16a), (16b) and accordingly, they can be calculated on the basis of Eqs. (17) and (18) for the ferroelectric and paraelectric phases respectively because the average values coincide with the properties profiles amplitude. As an illustration, we depicted in Figs. 6 and 7 the temperature dependence of the inverse dielectric susceptibility and pyrocoefficient, the latter being proportional to the spontaneous polarization (see Eq. (17a)). In Figs. 6, 7 we introduced $P_{s0}(0) = \sqrt{\alpha_0 T_c / \beta}$, $\chi_0(0) = 1/(\alpha_0 T_c)$ and $\Pi_0 = \sqrt{\alpha_0} / (2\sqrt{\beta T_c})$ which are these properties at $T = 0$ in the bulk material. The thickness dependencies are depicted in the insets to Figs. 3, 4, 5. In particular, the slope of the strait line in the inset to Fig. 4 gives the value of the parameter $2Kl_d/l_c$ that defined both susceptibility, pyrocoefficients and polarization (see Eq. (17b) and inset to Fig. 5).

A characteristic feature of the properties temperature dependencies is the shift of the average properties anomalies to lower temperature on decreasing the film thickness. Since

the divergences of χ and Π are related to the temperature of the thickness induced ferroelectric phase transition (see Eqs. (17), (18)), the aforementioned shift is related to the T_{cl} dependence on the film thickness (see Fig. 1). The shift of T_{cl} due to the depolarization field effect (compare dashed and solid lines in Fig. 1) defines this field effect on the average properties of the ferroelectric films. Since the intersections of the curves with abscissa axis in Fig. 1 defines the $l_c(0)/l_0(0)$ value, the shifts of $l_c(0)/l_0(0)$ to larger values due to the depolarization field contribution is clearly seen.

The estimations of $l_0(0) = \sqrt{\delta/(\alpha_0 T_c)}$ and $l_d = \sqrt{\delta/(4\pi)}$ values for the parameters of PbTiO_3 and BaTiO_3 [3,5] gave respectively $l_0(0) = 15 \text{ \AA}$, $l_d = 0,6 \text{ \AA}$ and $l_0(0) = 40 \text{ \AA}$, $l_d = 2 \text{ \AA}$ which makes it possible to obtain the $l_c(0)$ value from the intersections in Fig. 1 or by the calculation of l_c on the basis of Eq. (8). For instance, for extrapolation lengths $\lambda_1 = \lambda_2 = l_0(0)$ $l_c(0) = 30 \text{ \AA}$ and 80 \AA with depolarization field contribution and without it $l_c(0) = 24 \text{ \AA}$ and 63 \AA for PbTiO_3 and BaTiO_3 respectively. Critical thickness has to increase with decrease of λ_1 and λ_2 values and at $T \neq 0$ namely $l_c(T) = l_c(0)/(1 - T/T_c)$ (see Eq. (8)). Because of the scattered δ values given in different works, the obtained l_c values should be considered as estimations only. But it is obvious that the larger T_c the smaller l_c .

An estimation of the T_{cl} value from Fig. 1, e.g. for $l/l_0(0) = 10$ and parameters of curve 2, gives $T_{cl} = 0,8T_c$ for the films with thickness 200-500 \AA . Therefore for such thin films the shift $\Delta T_c = T_c - T_{cl} = 0,2T_c$ and, e.g., for BaTiO_3 and PbTiO_3 , $\Delta T_c = 24^\circ \text{ C}$ and $\Delta T_c = 108^\circ \text{ C}$ respectively, which means that T_{cl} can be rather close to the T_c value. For thicker films T_{cl} is expected to be even closer to T_c (see Fig. 1).

C. The depolarization field and its influence on the physical properties

The depolarization field is given by Eq. (3), which after substitutions $P_z = P(1 - \varphi(\xi))$ and $\langle P \rangle = P(1 - A_1)$ (see section 4) can be rewritten as

$$E_z^d(\xi) = -4\pi P(A_1 - \varphi(\xi)). \quad (19)$$

Although A_1 value is small, it cannot be neglected in the region where $\varphi(\xi) = 0$ (see Eq. (10)). In particular in the very center of the film:

$$E_z^d \equiv E_z^d(\xi = h/2) = -4\pi P A_1. \quad (20a)$$

Allowing for $A_1 = l_d(U_1 + U_2)/l$ one can rewrite Eq. (20a) with respect to (17b) as:

$$E_z^d = -K \frac{l_d}{l} \sqrt{\frac{K}{\beta} \frac{l_d}{l_c} \left(\frac{l_c}{l} - 1 \right)} \quad (20b)$$

or

$$E_z^d = -\sqrt{\frac{\alpha_0}{\beta} (T_{cl} - T)} \alpha_0 (T_c - T_{cl}). \quad (20c)$$

Equations (20b) and (20c) should be applied when considering E_z^d thickness or temperature dependencies respectively.

It is clearly seen that $E_z^d = 0$ at $T = T_{cl}$ for arbitrary l and $l = l_c$ and $l \rightarrow \infty$ for arbitrary T . Between $l = l_c$ and $l \rightarrow \infty$, the absolute value of E_z^d achieves a maximum at $l_m = \frac{3}{2}l_c$. The value of depolarization field at this point is equal to $E_m^d = \frac{2}{3\sqrt{3}}\alpha\sqrt{-\alpha/\beta} = E_{c0}$, where E_{c0} is the coercive field of the bulk material. Near the surfaces, when $\varphi(\xi) \neq 0$ (see Eq. (10)), the small quantity A_1 can be neglected and E_z^d becomes thus positive, its profile being defined by the $\varphi(\xi)$ dependence. The point ξ_{cr} at which the change of depolarization field sign takes place can be obtained easily from Eq. (19), with $E_z^d(\xi_{cr}) = 0$ at $\varphi(\xi_{cr}) = A_1$. With respect to Eq. (10) this gives $(1 + U_2/U_1)l_d/l = \exp(-\xi_{cr})$ or $-\xi_{cr} = \ln(l_d/l) + \ln(1 + U_2/U_1)$. Keeping in mind that $l/l_d = h \gg 1$, and that U_1 and U_2 are quantities of the same order of magnitude (e.g. $U_2/U_1 = 1$ at $\lambda_1 = \lambda_2$) one can conclude that for symmetrical boundary conditions

$$\xi_{cr} = \ln \frac{l}{2l_d}. \quad (21)$$

Therefore at $\xi < \xi_{cr}$ $E_z^d(\xi) > 0$, while $E_z^d(\xi) < 0$ at $\xi > \xi_{cr}$. Similar conditions on the right hand side of the film can be obtained by substitution of $(h - \xi_{cr})$ for ξ_{cr} in Eq. (21).

To illustrate the E_z^d behaviour we have represented its profile and the thickness dependence of $E_z^d(z = l/2)$ in the inset b) of Fig. 8. One can see that, because there is no

depolarization field in the film center at critical thickness, E_z^d increases on increasing l/l_c , achieves maximum at $l_c/l_m = \frac{2}{3}$ and at $l \rightarrow \infty$ $E_z^d \rightarrow 0$ again. More details for the region $E_z^d(\xi) < 0$ are given in inset a).

The effect of the depolarization field is clearly shown in Figs. 3 to 5. The dashed lines are the profiles calculated without any depolarization field contribution following the way described in Appendix for the thinnest (curve 1) and the thickest (curve 5) films. It can be seen that this field influence depends on the film thickness: the thinner the film the stronger the change in the profile shape. Comparison of solid and dashed curves in Figs. 3, 4, 5 shows that the depolarization field increases χ and Π values, but decreases the P value for the thin film close to the critical thickness, while for thick films, a decrease in χ and Π and an increase in P_s are observed in most part of the film (see curve 5). It is worth to notice that the dashed curves in Figs. 4, 5 display small maxima near the surfaces contrary to solid curves which remains flat. It is clear that the influence of the depolarization field on the polarization is directly related to the peculiarities of depolarisation field profile (see Fig. 8). In particular the positive sign of $E_z^d(\xi)$ in the tiny regions close to the surfaces and negative sign outside these regions explains the increase of the spontaneous polarization near the surfaces and its decrease in most part of the film, leading to the flattening of the polarization (see Fig. 3). The difference in the behaviors induced by the depolarization field effect on P_s on one hand, and χ and Π , which are the derivative of P_s , on the other hand, is not surprising, since, e.g., $\Pi \sim 1/P_s$, and an increase in P_s should result in a Π decrease and vice versa.

VI. DISCUSSION AND CONCLUSION

Let us discuss briefly the accuracy of the calculations and the physical model we used here. The variational method used for the calculation of the polarization in the ferroelectric phase is an approximation, its accuracy being usually a few percent. To prove this we performed the calculations in two important cases by other exact ways: in the vicinity of

the phase transition, where P_s tends to zero and can be considered as a small parameter, and for the thick film limit, when the polarization space distribution is almost uniform. The solutions obtained by these methods are reported in the inset of Figs. 3, 4, 5 by dashed and dotted-dashed lines. It can be seen that these lines coincide with those obtained by the variational method with a good accuracy.

In our calculations we did not take into account the possible shift of T_c by mechanical strains originating from the misfit between the substrate and the film lattice constants, thermal expansion coefficients and growth imperfections. Because of the strain relaxation due to misfit dislocations, the strains are not homogeneous and in the general case their value are small in most part of the film [16]. We accordingly neglected the renormalization of T_c value by mechanical strains.

Let us discuss briefly the depolarization field effect. As it follows from the above considerations, the depolarization field does not change the general form of P_s , χ and Π average values dependences on the film thickness and temperature (see Figs. 6, 7). The depolarization field smoothes the space distributions of these quantities, and in particular cancels the maxima near the film surfaces in the space distributions of χ and Π obtained in the case where the depolarization field can be neglected (see Figs. 4, 5).

The main effect of the depolarization field is the shift of the boundary between the paraelectric and ferroelectric phases on the temperature - film thickness phase diagram to larger thickness, as can be seen from Fig. 1. This shift can be especially large for thin films because the critical temperature T_{cl} obeys a $T_c - T_{cl} \sim 1/l$ dependence when taking into account depolarization field contribution (see Eq. (9) and solid lines in Fig. 1) but a $T_c - T_{cl} \sim 1/l^2$ without this contribution (see Eqs. (A6a), (A6b) and dashed lines in Fig. 1). Because of that a scattering of experimental critical values can be expected for films produced in different technological conditions and from materials with different degrees of purity. These factors might influence the domain structure and conductivity of the film and consequently the depolarization field.

Obviously depolarization field effects in thick films under short-circuit conditions can

be neglected in most part of the film except close to the surfaces. But another important case where the contribution of the depolarization field can be neglected is related to the conditions on the film surfaces. More particularly, for extrapolation lengths much larger than the correlation length l_0 it follows from Eq. (A6c) that $T_c - T_{cl} \sim 1/l$ and Eq. (A6c) looks like Eq. (9).

Although we considered spontaneous polarization and other properties without Any external electric field application, the case of $E \neq 0$ can be considered on the basis of Eq. (13), i.e., in the same way as nonlinear effects in the bulk. It should be mentioned that a nonlinear dielectric response was measured in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films with thickness 24-160 nm [8]. Authors of this work explained the observed temperature and E -field dependencies using a conventional power series expansion of the free energy. They came to the conclusion that only the first term of this power series varies significantly with the film thickness or the temperature. This conclusion is in very good agreement with the results obtained in our work. The spatial distribution of the pyroelectric coefficient measured by LIMM method in homogeneously poled ferroelectric polymer films [17] looks like that depicted in Fig. 5. This may give some support to the relevance of the calculated profiles of polarization and dielectric susceptibility.

The obtained results pave the way to calculations of ferroelectric film properties using a conventional minimization of the free energy for bulk material, but with renormalized coefficient before squared polarization. This renormalized coefficient includes the contribution of polarization gradient, depolarization field, polarization at the surface and the characteristics of the bulk material. Because this coefficient has been shown to depend on the critical parameters of the thickness induced ferroelectric phase transition T_{cl} and l_c in the same way as this coefficient temperature dependence in the bulk, namely, for the films, $a = \alpha_0(T - T_{cl})$ or $a = Kl_d/l_c(l_c/l - 1)$ (see Eq. (16)), this makes it possible to obtain these critical parameters through the observation of thermodynamic properties anomalies, e.g. by measurements of the average dielectric susceptibility maximum position at different temperatures at fixed thickness or at fixed temperature and different film thickness respectively. The novel ap-

proach developed here is suitable for the calculation of the profiles and average values of the polarization, dielectric susceptibility, pyrocoefficient, entropy, specific heat etc. In order to calculate the electromechanical properties, we have to include into the free energy functional the interaction of the non homogeneous polarization with external strains. This consideration is in progress now.

VII. APPENDIX

In order to discuss the influence of the depolarization field, let us consider briefly the model without taking into account that field. In this case the equation giving the space distribution of polarization as a function of the thickness of the film has the form Eq. (2a) without the last two terms. This equation has a nontrivial solution when the electric field is zero. In the case of boundary conditions (2b) with positive extrapolation lengths, this solution exists only under the condition $\alpha < 0$ (see, e.g. [18]) and gives the following space distribution of the spontaneous polarization for the phase transition of the second order:

$$P_s(z) = P_{s0} \sqrt{\frac{2m}{1+m}} \operatorname{sn} \left(\frac{z + z_0}{l_0 \sqrt{1+m}} \middle| m \right) \quad (\text{A1})$$

Here $l_0 = \sqrt{-\lambda/\alpha}$ is the correlation length, $\operatorname{sn}(u|m)$ is the elliptic sine function [18], and the constants m and z_0 have to be determined from the boundary conditions (2b). Using the properties of the elliptic functions it is easy to obtain equations which these constants satisfy:

$$z_0 = l_0 \sqrt{1+m} F(\arcsin(f_1), m) \quad (\text{A2})$$

$$l = l_0 \sqrt{1+m} (2K(m) - F(\arcsin(f_1), m) - F(\arcsin(f_2), m)) \quad (\text{A3})$$

where $K(m)$ and $F(\phi, m)$ are complete and incomplete elliptic integrals of the first kind respectively [18], and the following definition is introduced:

$$f_i \equiv f(m, \lambda_i) = \sqrt{\frac{1+m}{2m} \left(1 + \left(\frac{l_0}{\lambda_i} \right)^2 - \sqrt{\left(1 + \left(\frac{l_0}{\lambda_i} \right)^2 \right)^2 - \frac{4m}{(1+m)^2}} \right)} \quad (\text{A4})$$

The parameter m varies from 0 to 1 in Eqs. (A1) - (A4), otherwise the spontaneous polarization would be a complex number. As it follows from Eq. (A3) with the condition $m \rightarrow 0$, thickness l tends to some critical value l_c which corresponds to a zero value of the spontaneous polarization (A1). When the thickness of the film is less than critical, the spontaneous polarization vanishes. The critical thickness for the considered case $\lambda_1 \geq 0, \lambda_2 \geq 0$ has the form:

$$l_c = l_0 \left(\pi - \arctg \left(\frac{\lambda_1}{l_0} \right) - \arctg \left(\frac{\lambda_2}{l_0} \right) \right) \quad (\text{A5})$$

The critical temperature T_{cl} for a film with thickness l can be found from the condition $l = l_c(T = T_{cl})$, which results in a transcendental equation for the dependence of T_{cl} on the film parameters. This equation can be simplified in several limiting cases. When the phase transition temperature is much smaller than in the bulk ferroelectric ($T_{cl} \ll T_c$), i.e., for very thin films, the following dependence can be obtained:

$$T_{cl} = T_c \left(1 - \left(\frac{l_c(0) + l_0(0) (g_1 + g_2)}{l + l_0(0) (g_1 + g_2)} \right)^2 \right), \quad l - l_c(0) \ll l_0(0) \quad (\text{A6a})$$

Here $l_c(0)$ and $l_0(0) = \sqrt{\lambda/(\alpha_0 T_c)}$ are the critical thickness and correlation length respectively at zero temperature $T = 0$, and $g_i = \lambda_i / \sqrt{l_0^2(0) + \lambda_i^2}$.

When the phase transition temperature is of the same order of magnitude as in the bulk ferroelectric ($T_{cl} \approx T_c$), i.e. for films with large thickness, it is easy to get from Eq.(A5) the following expression:

$$T_{cl} = T_c \left(1 - \left(\frac{\pi l_0(0)}{l + \lambda_1 + \lambda_2} \right)^2 \right), \quad l \gg l_0(0) \quad (\text{A6b})$$

Note that this expression is also valid in the whole temperature and thickness ranges for extrapolation lengths much smaller than the correlation length ($\lambda_i \ll l_0$). In the opposite case, i.e. $\lambda_i \gg l_0$, the critical temperature is expressed as:

$$T_{cl} = T_c \left(1 - \frac{l_0^2(0)}{l} \left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right) \right), \quad \lambda_i \gg l_0 \quad (\text{A6c})$$

Since $\alpha = \alpha_0(T - T_c)$, where T_c is the temperature of the ferroelectric phase transition of the thick film, the nonhomogeneous polarization of the film $P(z)$ should depend on temperature T and external electric field E . This allows to calculate the non homogeneous pyrocoefficient $\Pi(z) = (dP(z)/dT)_{E=0}$ and the linear dielectric susceptibility $\chi(z) = (dP(z)/dE)_{E=0}$. Differentiation of Eqs. (2a) and (2b) gives the following differential equations for the pyrocoefficient and dielectric susceptibility calculations:

$$(\alpha + 3\beta P_s^2)\Pi - \delta \frac{d^2\Pi}{dz^2} + \alpha_0 P_s = 0; \quad (\text{A7a})$$

$$\left. \frac{d\Pi}{dz} \right|_{z=0} = \frac{\Pi}{\lambda_1} \Big|_{z=0}; \quad \left. \frac{d\Pi}{dz} \right|_{z=l} = - \frac{\Pi}{\lambda_2} \Big|_{z=l} \quad (\text{A7b})$$

$$(\alpha + 3\beta P_s^2)\chi - \delta \frac{d^2\chi}{dz^2} - 1 = 0; \quad (\text{A8a})$$

$$\left. \frac{d\chi}{dz} \right|_{z=0} = \frac{\chi}{\lambda_1} \Big|_{z=0}; \quad \left. \frac{d\chi}{dz} \right|_{z=l} = - \frac{\chi}{\lambda_2} \Big|_{z=l} \quad (\text{A8b})$$

The general solution of Eq. (A8a), which is a particular case of the Lamé equation, is the following [19]:

$$\Pi(x) = C_1^{py} y_1(x) + C_2^{py} y_2(x) + y_3^{py}(x) \quad (\text{A9})$$

where the function $y_i(x)$ has the following form:

$$y_1(x) = cn(x, m) dn(x, m), \quad (\text{A10a})$$

Here $cn(u|m)$ and $dn(u|m)$ are the elliptic cosine and delta amplitude functions respectively [18]

$$y_2(x) = \left(x - \frac{1+m}{1-m} E(am(x), m) \right) \frac{y_1(x)}{1-m} + y_0(x) \frac{1+m^2 - m(1+m) y_0^2(x)}{(1-m)^2}, \quad (\text{A10b})$$

$$y_3^{py}(x) = -\Pi_m \left(\left(x - \frac{2 E(am(x), m)}{1-m} \right) y_1(x) + y_0(x) \frac{1+m - 2m y_0^2(x)}{1-m} \right)$$

$$\Pi_m = \Pi_0 \frac{\sqrt{2m(1+m)}}{1-m}, \quad \Pi_0 = \frac{dP_0}{dT}. \quad (\text{A10c})$$

Here Π_0 is the thick film pyroelectric coefficient and the following definitions are introduced:

$$x = \frac{z + z_0}{l_0 \sqrt{1 + m}}, \quad y_0(x) = sn(x, m).$$

In Eqs.(A10b, c) $E(\varphi, m)$ and $am(x)$ are an incomplete elliptic integral of the second kind and an elliptic amplitude function respectively [18]. The constants C_1^{py} and C_2^{py} are omitted because of their cumbersome expression.

The dielectric susceptibility can be obtained in a similar way:

$$\chi(x) = C_1^{ch} y_1(x) + C_2^{ch} y_2(x) + y_3^{ch}(x) \quad (\text{A11})$$

where

$$y_3^{ch}(x) = -2\chi_0(1 + m) \frac{1 + m - 2m y_0(x)}{(1 - m)^2}, \quad (\text{A12})$$

Here $\chi_0 = -1/2\alpha$ is the thick film susceptibility. Coefficients C_1^{ch} and C_2^{ch} differ from C_1^{py} and C_2^{py} in Eq.(14) because of the difference between $y_3^{py}(x)$ and $y_3^{ch}(x)$.

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V. 3.

FIGURES

FIG. 1. The dependence of the critical temperature T_{cl} on the film thickness (logarithmic scale) for $f(0) = \alpha_0 T_c / 4\pi = 0.01$ and for different extrapolation lengths values: $(\lambda_1/l_d, \lambda_2/l_d) = (0.5, 0.6)$, $(5, 3)$, $(10, 6)$ for lines 1, 2 and 3 respectively with (solid lines) and without (dashed lines) the depolarization field contribution. The behavior as a function of the reciprocal film thickness is given in the inset.

FIG. 2. The dimensionless critical thickness fl_c/l_d in the (d_1, d_2) space. The d_i 's are the dimensionless extrapolation lengths. The critical thickness is given as numbers close to the relevant plots.

FIG. 3. The space distribution of the spontaneous polarization P_s as a function of the z coordinate for the following values of parameters: $f = 0.01$, $\lambda_1/l_d = 5$, $\lambda_2/l_d = 3$, and for different values of the film thickness $l/l_c = 1.01, 1.04, 1.16, 1.7, 4$ (solid curves 1 - 5 respectively). The dashed curves 1 and 5 represent the space distribution of P_s calculated without taking into account the depolarization field. The average value of P_s^2 vs the reciprocal film thickness l is represented in the inset. The solid line represents the dependence obtained using the variational method, dashed and dash-dotted curves are obtained by expansions close to the phase transition and for the thick films respectively.

FIG. 4. The space distribution of the dielectric susceptibility in the ferroelectric phase as a function of the z coordinate for the same values of parameters as those in Fig. 3. The dashed curves 1 and 5 represent the dielectric susceptibility space distribution calculated without taking into account the depolarization field. The inset gives the dependence of the reciprocal averaged dielectric susceptibility as a function of the reciprocal thickness of the film. The meaning of the solid, dashed and dash-dotted curves is the same as in Fig.3.

FIG. 5. The space distribution of Π as a function of the z coordinate for the same values of parameters as those in Fig. 3. The dashed curves 1 and 5 represent the Π space distribution calculated without taking into account the depolarization field. The inset gives the dependence of the reciprocal averaged Π as a function of the reciprocal thickness of the film. The meaning of the solid, dashed and dash-dotted curves is the same as in Fig.3.

FIG. 6. The temperature dependence of the reciprocal averaged dielectric susceptibility for the following values of parameters: $f(0) = \alpha_0 T_c / 4\pi = 0.01$, $\lambda_1 / l_d = 5$, $\lambda_2 / l_d = 3$, and for different values of the film thickness $l / l_c(0) = 1.11, 1.43, 2, 3.33, 10$ (curves 1 - 5 respectively). The dashed line depicts the temperature dependence of the bulk ferroelectric reciprocal dielectric susceptibility $\chi_0(T)$. The temperature dependence of the average dielectric susceptibility for the same values of parameters is given in the inset, where the dashed line represents the bulk ferroelectric dielectric susceptibility.

FIG. 7. The temperature dependence of the averaged spontaneous polarization for the same values of parameters as those in Fig. 6. The temperature dependence of the bulk ferroelectric spontaneous polarization T / T_c is plotted as a dashed line. The temperature dependence of the averaged Π for the same values of parameters is given in the inset, where the dashed line represents the bulk ferroelectric pyroelectric coefficient $\Pi_0 = dP_{s0} / dT = \Pi_0(0) \sqrt{1 - T / T_c}$.

FIG. 8. The space distribution of the depolarization field close to the film surface for the following values of parameters: $f = 0.01$, $\lambda_1 / l_d = 5$, $\lambda_2 / l_d = 3$, and for different values of the film thickness $l / l_c = 1.01, 1.1, 1.5, 4$ (curves 1 - 4 respectively). The region of the plot where the depolarization field is negative is depicted in the inset (a). The depolarization field in the center of the film as a function of the reciprocal film thickness is depicted in the inset (b) for the parameters values given above.















